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ORGANIC DERIVATIVES OF HETEROPOLY MOLYBDATES. (U)

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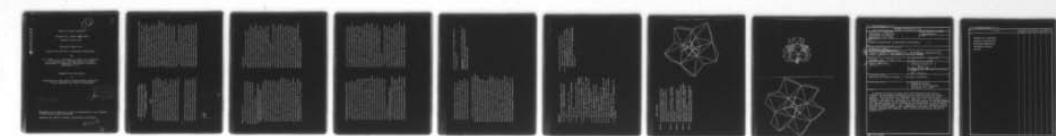
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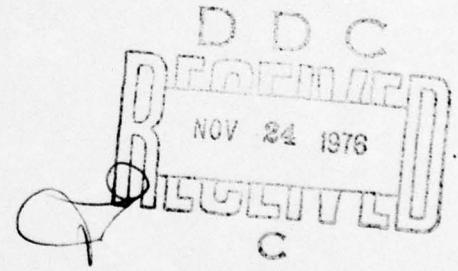
by

M.T. Pope\*, C.O. Quicksall, W. Kwak, L.M. Rajdović,  
J.K. Stalick, K.M. Barkigia and T.F. Scully  
Department of Chemistry, Georgetown University,  
Washington, D.C.

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Organic Derivatives of Heteropoly Molybdates

M.T. Pope\*, C.O. Quicksall, W. Kwak, L.M. Rajkovic,  
J.K. Stalick, K.M. Barkigia and T.F. Scully

Department of Chemistry, Georgetown University,  
Washington, D.C. 20057 USA

Summary

A survey is given of recent work that characterizes several examples of heteropoly molybdates with covalently-attached organic groups. The structures of complexes with the following stoichiometries,  $(RP)_2Mo_5O_2^{4-}$ ,  $(RAs)_2Mo_6O_2^{4-}$ ,  $(RAs)_4Mo_12O_4^{8-}$ , and  $R_2AsMo_6O_{14}H^{2-}$  further illustrate the prevalence of cis MoO<sub>6</sub> groups in polymolybdates, and they also appear to be governed by the dimensions of the RP(As)O<sub>4</sub><sup>2-</sup> and R<sub>2</sub>AsO<sub>4</sub><sup>2-</sup> heterogroups. Novel features of the new complexes include optical activity based on the oxometallate structure of  $(RP)_2Mo_5O_2^{4-}$ , neutral zwitterionic species, and a localized non-acidic proton in  $R_2AsMo_6O_{14}H^{2-}$ .

also undergo a series of reversible electron transfer reactions to yield mixed valence (IV, VI) "heteropoly blues". It has been customary to represent the structures of heteropoly anions as assemblages of metal-oxygen polyhedra which share corners, edges and occasionally faces<sup>1,2</sup>, and to invoke electrostatic arguments ("Pauling's Rules") to rationalize bond-lengths and angles. However, in spite of the almost identical ionic radii of Mo<sup>6+</sup> and W<sup>6+</sup>, there are very few instances of isostructural heteropoly molybdates and tungstates. In general, molybdates tend to adopt structures in which each octahedrally coordinated molybdenum has two *cis* terminal oxo-oxygens (a notable exception is the Keggin structure for  $\alpha\text{-PMo}_{12}O_{40}^{3-}$ ) whereas tungstates seem to favor structures in which each metal atom has a single terminal oxygen atom. Only anions with the latter structural feature undergo reduction to give heteropoly blues<sup>3</sup>.

We have recently started to explore the possibility of synthesizing heteropoly complexes that would contain, in addition to the ionic oxometallate cluster, one or more covalently-attached organic groups. Such complexes would represent an entirely new class of compounds that would be expected to display novel combinations of properties, and would lead to applications in areas as diverse as organic synthesis, polymer chemistry, X-ray and electron microscope

Heteropoly molybdate (VI) and tungstate(VI) anions are typically 'ionic' oxometallate clusters of high symmetry, large size, and high ionic weight<sup>1</sup>. They are usually the anions of strong acids, they form salts that are soluble in a variety of aqueous and nonaqueous solvents, and they may

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labelling, and catalysis.

There are several possible routes to complexes of this type, and we summarize here our recent work characterizing new heteropoly molybdates in which the organic groups are directly bound to the heteroatoms. Four classes of such complexes have so far been identified.

1. Pentamolybdobisorganophosphonates,  $(RP)_2Mo_5O_{11}^{4-}$ , and Hexamolybdoisorganoarsonates,  $(RAs)_2Mo_6O_{14}^{4-}$ .

The 2:5 phosphonate<sup>4</sup> and 2:6 arsenate<sup>5</sup> complexes are rapidly formed when molybdate and the appropriate organic anion,  $RP_2O_7^{2-}$  or  $RAsO_4^{2-}$ , are mixed at pH 4-5. Both types of complexes are characterized by an absorption band at ca 250 nm, by slight downfield nmr shifts of the R-group protons compared with the uncomplexed acids, and by IR spectra. Salts of the phosphonate (2:5) complexes with  $R = H$ ,  $CH_3$ ,  $C_2H_5$ ,  $C_6H_5$ , and  $\text{C}_6\text{H}_4\text{NH}_3^+$  have been isolated, and the crystal structures of  $(\text{NH}_4)_2[(\text{CH}_3\text{P})_2\text{Mo}_5\text{O}_{11}] \cdot 5\text{H}_2\text{O}$  (II) were determined<sup>6</sup>. The anions in both structures contain a ring of five edge- and corner-shared  $\text{MoO}_4$  octahedra capped above and below by the RPO<sub>4</sub> tetrahedra as shown in Figure 1.

The same structural arrangement has been found in the molybdochosphate anions  $H_nP_2Mo_5O_{11}^{(6-n)-}$  which may be viewed as inorganic analogues ( $R = O^{2-}$ ,  $\text{OH}^-$ ) of the complexes

described here.<sup>7</sup>

The structure illustrated in Figure 1 is chiral. Compound I crystallizes in space group P2<sub>1</sub>, and the polarity of the crystal employed in the structure analysis was determined<sup>6</sup>. Although racemization of the optical isomers is expected to be very rapid in hydrolytic solvents,<sup>8</sup> it has been possible to precipitate a diastereomeric brucine salt of  $(C_6H_5P)_2Mo_5O_{11}^{4-}$  which is soluble and stable in acetonitrile. The solution in acetonitrile shows a negative Cotton effect for the 250-nm chromophore of the heteropoly anion as well as the expected optical rotatory dispersion of the brucine present.<sup>8</sup>

The arsonate (2:6) complexes,  $R = CH_3$ ,  $C_6H_5$ , and  $PC_6H_5NH_2$ , have the structure illustrated in Figure 2. The ring of six as opposed to five  $\text{MoO}_4$  octahedra is almost certainly a consequence of the larger size of arsenic over phosphorus. Recently, Pettersson<sup>9</sup> has proposed an analogous structure for the anion  $As_2Mo_6O_{14}^{6-}$  (=  $[\text{OAs}]_2Mo_6O_{14}^{6-}$ ). Several possibilities for derivatization of the 2:5 and 2:6 complexes may be envisaged, although the heteropoly structures are stable only at pH 2.5-5. Examples of novel zwitterionic species with the 2:5 structure are  $[(H_3N^+)_2Mo_5O_{11}^{4-}]^-$  (Compound II) and the neutral complex  $[(en)_2Co(H_2O)_2Mo_5O_{11}^{4-}]$  prepared from cis [ $Co(en)_2(H_2O)(HPO_4)$ ]<sup>+</sup>.

**2. Dodecamolybdotetrakisorganoarsonates,  $(RAs)_4Mo_{12}O_6^{4-}$**

In acidic solutions (pH ca. 0.5) the 2:6 arsonate complexes are converted to 4:12 species  $(RAs)_4Mo_{12}O_6^{4-}$ .

The 4:12 anions with  $R = OH^-$  were first prepared by Debray in 1874<sup>11</sup>, and shown to be tetrameric by Contant in 1973<sup>12</sup>. The crystal structure of the ammonium salt,  $(NH_4)_4[(HOAs)_4Mo_{12}O_6] \cdot 4H_2O$  has recently been reported<sup>13</sup> and the anion structure is shown in Figure 3. The anion has tetrahedral symmetry and may be viewed as an "inside out" Keggin structure with bridging  $HOAsO_4^{2-}$  groups. The central cavity, which appears to be empty, has an estimated radius of 1.43 Å. We have isolated organic derivatives with the 4:12 stoichiometry and  $R = CH_3$ ,  $C_2H_5OH$ ,  $C_6H_5$  and  $EC_6H_5NH_3^+$ . Although a crystal structure determination of one of these derivatives is not yet complete, IR and UV spectra of the new complexes are very similar to those of the Debray salt.

**3. Tetramolybdotetrakisorganoarsinates,  $R_2AsMo_4O_10H^{2-}$**

The 2:5, 2:6, and 4:12 complexes incorporate tetrahedral heteroatoms that have one of the four possible bridging oxygens replaced by an organic group. Organoarsinates,  $R_2AsO_4^-$ , have two such binding positions blocked. Complexes of molybdate(VI) with  $R_2AsO_4^-$  anions are formed at pH 4-5 and have the stoichiometry  $R_2AsMo_4O_10H^{2-}$ . The guanidinium

salt of the dimethyl derivative appears to be the same as a compound first prepared by Rosenheim and Bilecki<sup>14</sup> and formulated by them as  $(CN, H_4)_2H[As(OH)_2(CH_3)_2(Mo_2O_7)_2]$ . The crystal structure of  $(CN, H_4)_2[(CH_3)_2AsMo_4O_10H \cdot H_2O$  shows the anion as in Figures 4 & 5<sup>15</sup>. This is only the second example (after dcdecamolybdocerate<sup>16</sup>,  $CeMo_{12}O_10^{8-}$ ) of a polyanion structure that involves face-sharing of  $Mo_6$  octahedra. As might be expected the molybdenum atoms are displaced from the centres of their respective octahedra towards the unshared edges: metal-metal separations are 3.36 and 3.16 Å through shared edges and faces respectively. The compact structure of the anion is dictated by the steric requirements of the  $(CH_3)_2AsO_4^-$  group which suffers very little distortion from 'tetrahedral' symmetry ( $OAsO$  angle 106.6°).

The complexes are stable at pH 2-6 in aqueous solution and, with appropriate counterions, in organic solvents. All of the salts prepared contain two cations per anion and must be formulated with an extra proton. Direct evidence for the proton is provided by IR and NMR spectra of anhydrous salts such as  $(Bu_4N)_2[(CH_3)_2AsMo_4O_10H]$ . The IR spectra show a narrow line at  $3615 \text{ cm}^{-1}$  and the NMR spectra (in methylene chloride) a singlet with the appropriate intensity at ca. 2.2 ppm. The proton is not titratable but

undergoes rapid exchange in protic solvents. It is almost certainly located on the unique oxygen that bridges the four molybdenum atoms (see Figure 5) since this is likely to be the most basic. Furthermore the X-ray data for the guanidinium salt show a tightly bound water of hydration 2.8 Å from this particular oxygen.

The structures of the new heteropoly complexes further exemplify the prevalent structural feature for polymolybdates(VI), namely each molybdenum atom with two cis unshared oxo-oxygens<sup>3</sup>. Consequently, none of these complexes undergoes reversible one or two-electron reductions to heteropoly blue species, but all are irreversibly reduced to molybdenum(V) at the dropping mercury and wax-impregnated graphite electrodes. The structures are 'rational' in the sense that the dimensions of the heterogroups are virtually unchanged upon complexation. The nonbonded O.....O distances in  $\text{PO}_4^{3-}$  (2.53 Å) and  $\text{AsO}_4^{3-}$  (2.86 Å) match very closely the appropriate distances in the four heteropoly structures. A dialkylphosphinate,  $\text{R}_2\text{PO}_2^-$ , analogue of the 1:4 complex (Figure 4), could not be synthesized, presumably because the short OPO bridge would further compress the already closely packed structure. However, it may be noted that the dimensions of  $\text{SO}_4^{2-}$  and  $\text{SeO}_4^{2-}$  ( $\text{O} \cdots \text{O} = 2.41$  and 2.61 Å respectively<sup>17</sup>) are appropriate for the 2:5

structure and both  $\text{S}_2\text{Mo}_2\text{O}_11^{4-}$  and  $\text{Se}_2\text{Mo}_2\text{O}_11^{4-}$  complexes are well characterized.<sup>18</sup>

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Figure Captions

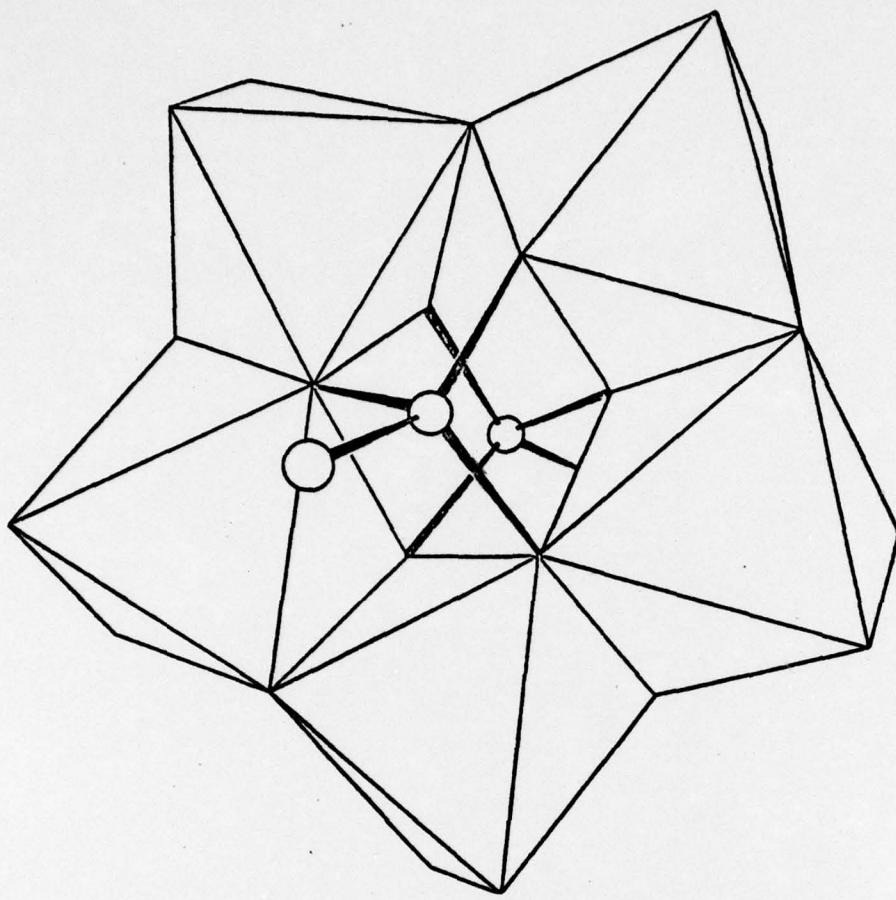
**Figure 1.** The structure of  $(\text{CH}_3\text{P})_2\text{Mo}_5\text{O}_{21}^{4-}$  (Stalick and Quicksall) showing arrangement of edge- and corner-shared  $\text{MoO}_6$  octahedra. The circles represent the phosphorus atoms and one of the methyl groups.

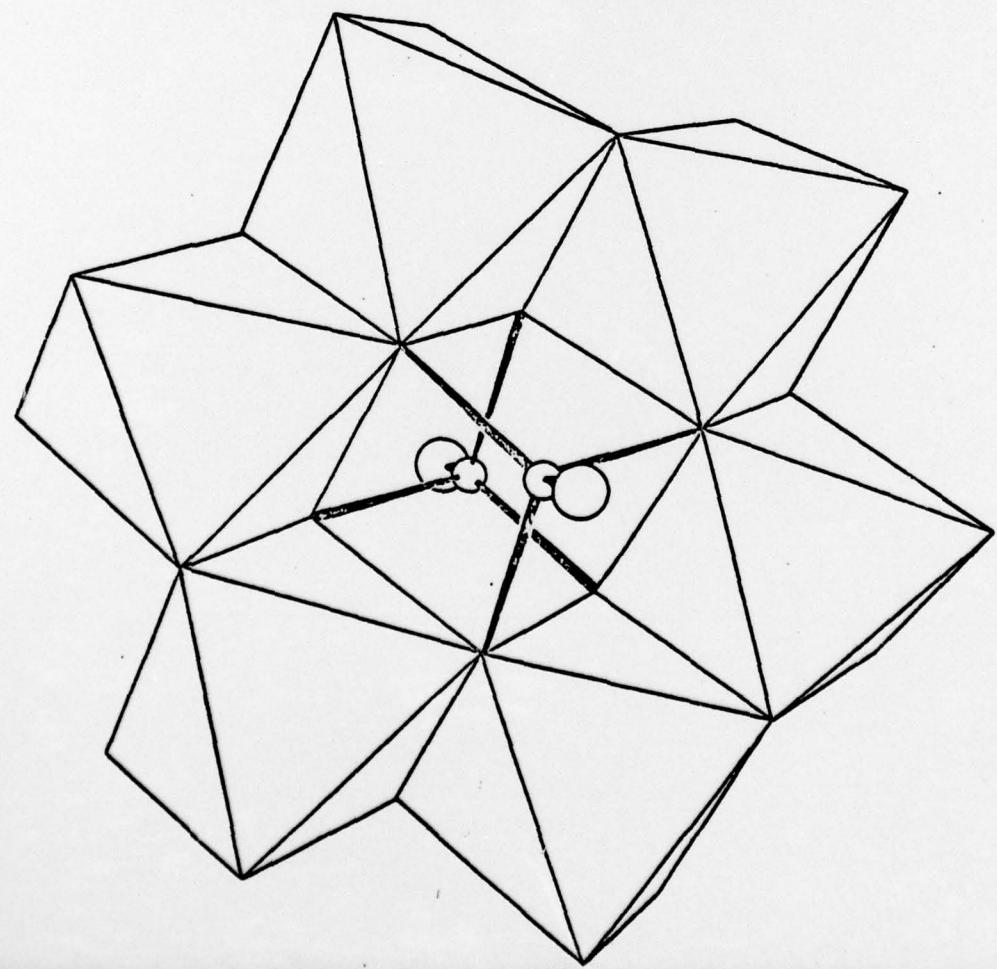
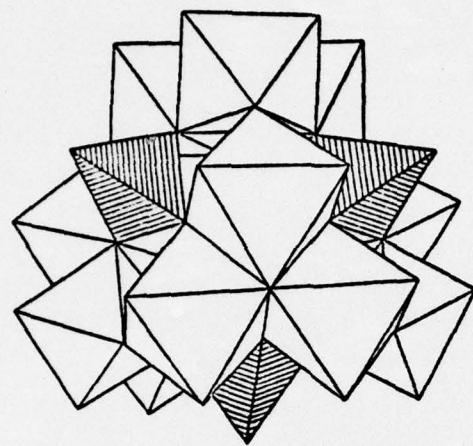
**Figure 2.** The structure of  $(\text{CH}_3\text{As})_2\text{Mo}_6\text{O}_{24}^{4-}$  (Kwak et al.). The circles represent the arsenic atoms and the methyl groups.

**Figure 3.** The structure of  $(\text{HOAs})_4\text{Mo}_{12}\text{O}_{46}^{4-}$  (Nishikawa and Sasaki). The free vertices of the  $\text{AsO}_4$  tetrahedra (shaded) are presumed to be protonated.

**Figure 4.** The structure of  $(\text{CH}_3)_2\text{AsMo}_4\text{O}_{15}\text{H}^{2-}$  (Barkigia et al.), showing edge- and face-shared  $\text{MoO}_6$  octahedra and  $(\text{CH}_3)_2\text{As}$  group (circles).

**Figure 5.** Another view of the structure of  $(\text{CH}_3)_2\text{AsMo}_4\text{O}_{15}\text{H}^{2-}$  showing the probable location of the proton.





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